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DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

MATERIALS RESEARCH LABORATORIES

MELBOURNE, VICTORIA

REPORT

MRL-R-796

A STATISTICAL EVALUATION OF
SOME PHYSICAL AND CHEMICAL CHARACTERISTICS
OF OCEAN WATER AT TWO STATIONS OFF THE
EAST AUSTRALIAN COAST

J.H. Bishop,* A. de Forest, R.W. Pettis, A.T. Phillip and P.D. Watt

Approved for Public Release

* Principal author, to whom all enquiries should be addressed

SEPTEMBER, 1980

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ABSTRACT

Salinity, pH, dissolved oxygen, temperature, Mg, Cd, Cu, Pb and Zn were
measured at depths down to 3600 m at two stations located at latitude 31° 58'S,
longitude 154° 02'E and latitude 30° 20'S, longitude 154° 40'E. The heavy metal
concentrations (Cd < 0.2 μgl^{-1}; Cu 0.4 - 4.8 μgl^{-1}; Pb 0.2 - 1.9 μgl^{-1}; Zn 0.4 -
7.6 μgl^{-1}) were typical of open ocean waters. The observed variations were within
the experimental error of the ASV method used, except in the surface waters of the
second station where a significant variation in copper concentration, which
correlated with a variation in lead concentration, was observed in conjunction with
a more variable pH. These variations were tentatively attributed to the possible
presence of a larger, or more variably distributed, biomass. Mg/Cl ratios, derived
from atomic absorption spectroscopic measurements, varied from 0.0643 to 0.0659,
the magnitude of the variation being similar to that found by other workers using
this technique. A number of correlations were found at both stations between depth,
salinity, temperature pH, dissolved oxygen saturation and magnesium. These
correlations demonstrated the feasibility of predicting chemical conditions at a
given location and depth more closely than is currently possible. It was found that
the relationships between these parameters were best expressed by simple linear
regression equations. Significant differences between near surface waters at the
two stations in some of these relationships showed that it would be necessary to take
the presence of hydrological features, such as thermal eddies, into account when
making such predictions.

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16. ABSTRACT (if this is security classified, the announcement of this report will be similarly classified):

        Salinity, pH, dissolved oxygen, temperature, Mg, Cd, Cu, Pb and
Zn were measured at depths down to 3600 m at two stations. The heavy
metal concentrations were typical of open ocean waters. A number of
correlations were found at both stations between depth, salinity,
temperature, pH, dissolved oxygen saturation, and magnesium.

C O N T E N T S

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1. INTRODUCTION

The service lives of materials are affected by the physical and chemical characteristics of the seawater in which they are immersed. The rates of degradation of most antifouling coatings, for instance, are particularly dependent upon flow conditions, salinity, temperature, pH, dissolved oxygen concentration and carbon dioxide concentration [1,2,3]. These characteristics are also the most significant chemical factors involved in the degradation of plastics and the corrosion of metals [4].

The objective of this investigation was to determine the extent to which these chemical and physical characteristics, with the exception of flow, were inter-related in ocean water off the East Australian Coast and to evaluate the extent to which these characteristics can be calculated either from relatively commonly available measurements or from a knowledge of the hydrology of a particular area. Studies have already shown that salinity in the South East Indian Ocean region can be derived from temperature data, particularly at depths greater than 75 metres [5]. The main hydrological features to be considered are the different water masses present [6,7,8] long term variations [9], short term fluctuations occurring as a result of eddy formation [10-15], seasonal variations [9,13] and changes due to influxes of slope water onto the continental shelf [16].

In addition to the parameters already mentioned, magnesium and heavy metal concentrations were included in this study. Magnesium causes sound attenuation in seawater at frequencies below 100 kHz [19,20] and it has been concluded from variations in this attenuation that there are significant differences in the chemical composition of the oceans [21,22]. Atomic absorption spectroscopy was chosen for magnesium analysis even though previous results obtained by this method [23,24] are apparently at variance with results obtained by titrimetric methods [25]. The much greater variations in Mg:Cl ratio found by atomic absorption spectroscopy have been attributed to unknown analytical error [26] but it was anticipated that more modern instrumentation and methods, coupled with a larger number of determinations, would either reduce the error in this method to acceptable levels or suggest the reason for this variability.

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The heavy metal determinations reported in this paper were carried out to provide detailed heavy metal data for a range of depths for comparison with other parameters and also base line data for heavy metal concentrations off the East Australian coast. Some data have been published for heavy metal concentrations in Australian rivers [27,28,29] and for surface waters off the East Australian coast [30,31,32] but there is still a paucity of data, particularly for deep waters.

2. EXPERIMENTAL METHODS

2.1 Sampling

Five litre PVC Niskin bottles, pre-treated by soaking in acidified seawater (pH 1.5) for 14 days before use, and 1.3 litre Nansen bottles were used. Where Niskin bottles were not fitted with reversing thermometers, they were paired with Nansen bottles.

Heavy metal samples were drawn only from the Niskin bottles. Samples were transferred from the sampling bottles to pre-aged 1 litre polyethylene bottles and acidified to pH 1.5 by the addition of 2 ml of 'Merck Suprapur' nitric acid. The need for adequately cleaned storage containers has been described in more detail elsewhere [39]. The samples were analysed in the ship's laboratory within 2 hours of collection.

Seawater temperatures and sampling depths were measured, calculated and corrected according to the standard procedures using deep sea reversing thermometers [37]. Duplicated thermometers were read to $0.01^{\circ}C$, the corrected readings agreeing to $0.01^{\circ}C$.

2.2 Dissolved Oxygen

Dissolved oxygen concentrations were determined using the Winkler titration [33] on samples removed from the sampling bottles and stabilized with all of the usual precautions as soon as possible after collection. The titrations were completed within 12 hours of sampling. The percentage saturation of dissolved oxygen was computed from the dissolved oxygen concentration and associated temperature and salinity measurements, using the equation of Weiss [34].

2.3 pH and Total Alkalinity

A Radiometer PHM 26 pH meter was used, calibrated with Beckman buffer solutions (pH 7 with a relative accuracy of ±0.03 pH units, pH 4 with a relative accuracy of ±0.01 pH units). Reproducibility was better than ±0.005 pH units. Buffer solutions and samples were equilibrated at $25^{\circ}C$ before pH measurements were made. The pH values of seawater samples were measured within 2 hours of collection and corrected for depth and temperature changes according to Strickland and Parsons [35]. Total alkalinity was determined by the method of Anderson and Robinson [35,36] with an error estimated to be ±0.02 meqv litre^{-1}.

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2.4 Salinity

Salinities were measured to 5 significant figures using an inductively coupled salinometer [33]. The results have been reported to 4 significant figures.

2.5 Magnesium Concentrations

Magnesium was determined using a Varian Techtron AA6 atomic absorption spectrometer using Parker's [38] method. The samples were diluted ten-fold with distilled water and an air-acetylene flame used with the burner at an angle to the light path to give optimum sensitivity and stability and the monochrometer set for the 202.5 nm line. Ten replicate analyses were carried out on each sample, the results being averaged. The standard deviation for ten replicate determinations carried out by this procedure was found to be 8·0, corresponding to 95% confidence limits of ±5·7. This method was found to be slightly more precise than the method of Fabricand et al. [23]. The greater sample dilution required in this method also resulted in less convenient sample manipulation.

2.6 Analysis of Heavy Metals

Analyses were carried out on all seawater samples for labile copper, lead, cadmium and zinc. The metals were analysed on board HMAS KIMBLA using anodic stripping voltammetry (ASV). A 9 ml aliquot of the seawater sample (pH 1.5) was added to an ASV quartz cell (previously cleaned in 1M HNO_3, and rinsed with doubly distilled water and sample immediately before analysis). The pH of the sample was adjusted to pH 4.5–5.0 by the addition of 1 ml of 1M sodium acetate/0.2M sodium chloride buffer. The buffer had been stripped of trace heavy metals by exhaustive electrolysis prior to use. This solution was deoxygenated with a stream of filtered, high purity nitrogen bubbling through the solution for five minutes; after this, the metals in the solution were deposited on a mercury graphite electrode at a potential of -0.9 v (versus a silver/silver chloride reference electrode), the sample being stirred by continued gas bubbling, for a period of 30 minutes. The anodic scan was then applied at a rate of 60 mv sec^{-1}, from -0.9 v to 0.0 v and the current-potential signals recorded on a Hewlett-Packard model 7004B X-Y recorder. ASV waves were observed at: -0.668 v (Cd), -0.510 v (Pb), -0.180 v (Cu). Quantification was by standard additions (47) and peak height measurement. An ESA Model 2011 anodic stripping voltammeter was used. The MCGE working electrode was prepared according to the method of Matson et al. [40].

Zinc was analysed in a similar manner, except that the pH of the sample was adjusted to 6.0–6.5 and the metal was deposited at -1.260 v for 30 minutes and the anodic scan was applied from -1.260 v to 0.0 v. The current-potential peak was again used to determine the concentration of zinc present in the sample. The zinc ASV wave was observed at -1.100 v.

Typical replicate analyses for heavy metals in seawater, obtained in the laboratory with the equipment used in this study, gave the results for the precision of the method listed in Table 1. (See [41] for further details).

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3. RESULTS

Station 1 was located at lat 31° 58' S, long. 154° 02' E. The 'Go-devil' messenger was dropped at 1153 K hours on 11 April 1975. Depth of water ≈4400 m. Station 2 was located at lat. 30° 20' S, long. 154° 40' E. The messenger was dropped at 1340 K hours on 12 April 1975. Depth of water ≈4600 m. Figure 5 shows the location of the stations in relation to the East Australia coast.

Results are shown in Tables 2 and 3.

4. ANALYSIS OF RESULTS

4.1 Statistical Analysis

The results were subjected to statistical analysis to determine:

(i) whether different water masses could be dis-tinguished on the basis of salinity, temperature, dissolved oxygen and depth data.

(ii) whether any of the parameters measured were correlated with any of the other parameters measured.

(iii) the relationship between correlated parameters and the accuracy with which one parameter could be calculated from the other.

(iv) whether any of the parameters measured varied either between the different water masses defined or between the two stations.

The statistical tests applied for inter-parameter correlation were:

(i) Calculation of correlation coefficients.

(ii) Linear regression analysis.

(iii) Comparison of regression coefficients.

The following tests were applied to grouped data for each parameter:

(i) 'Variance ratio' (F) test for comparison of variances.

(ii) 't' test for comparison of means, where the F test showed no significant difference in variance for the groups of data.

(iii) 'd' test for comparison of means [42,43] where the F test showed significant differences in variances for the groups of data.

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Where heavy metal concentrations were found to be $\leq x$ $\mu g.l^{-1}$, where x is the precision of the analytical method, arbitrary values of 0.5 x were assigned for the purposes of statistical analysis.

Temperature-salinity and dissolved oxygen-salinity plots suggested that the samples could be regarded as being taken from three bodies of water, the character of the water changing with depth, not geographical location. Table 4 lists the subdivisions chosen.

Statistical comparison of mean values of dissolved oxygen, salinity, temperature and σ_t (see Table 5 below) showed that, at the 95% level of confidence, water type A did not differ significantly between the two stations with respect to any of these parameters. Water type B differed from type A with respect to salinity, σ_t and temperature, while water type B differed from type C with respect to temperature and σ_t. Water type A also differed from type C with respect to dissolved oxygen concentration. The measurements obtained for each parameter were grouped according to the above water types, data for water type A being subdivided into 1A and 2A where significant differences in means or variances for a particular parameter were found between the 2 stations. Variance (F) ratios are tabulated in Table 6. The results of comparing means, using the 't' or 'd' test, are given in Table 5. Data source L denotes replicate analyses carried out to determine the variance of the analytical method used.

4.2 *Correlations Between Parameters and Comparison of Regression Coefficients*

Correlation coefficients for all possible combinations of the parameters measured are listed in Table 7. Values indicating a greater than 95% probability of correlation are underlined. Where correlation between pairs of parameters is indicated for both stations, the regression coefficients have been tested statistically [46] to determine whether there is any significant difference in the relationships between the parameters at the two stations. The results are listed in Table 8.

5. DISCUSSION

5.1 *Heavy Metal Concentrations*

A cursory examination of the results of the heavy metal analyses appeared to show that metal concentrations decreased with depth (Fig. 1).

Statistical analysis of the data for Cu, Pb and Zn did not support such a conclusion, however. Comparison of means (Table 5) showed no significant differences between the mean metal concentrations of the surface, intermediate and lower water masses (water types A, B and C) or between the two stations. There was no significant correlation between trace metal concentration and depth, or between trace metal concentration and any of the other measurements, except for correlations between the Mg/Cl ratio and zinc at Station 1, and between copper and lead at Station 2. These correlations are shown in Table 7.

Comparison of variances (Table 6) shows that the variations in measured trace metal concentrations were, with the exception of Cu at Station 2, not

statistically greater than the experimental error established from the results
of replicate analyses of a single sea water sample (Table 1) carried out ashore
as part of an inter-laboratory study [41]. Statistically significant
differences between the two stations are shown by the lead and copper variances,
the concentrations of both metals being more variable at Station 2 than at
Station 1. The significant correlation between these two metals at this station
indicates that the cause of this greater variability is the same for both metals.
This increased variability at Station 2 was also found with copper when comparing
results for the surface waters (water type A) at the two stations. Differences
in the plankton populations could account for this difference between the two
stations [18]. In the absence of supporting evidence, the correlation between
the Mg/Cl ratio and zinc at Station 1 must be attributed to coincidence only.

In addition to the differences in variances already discussed, the
variance of the lead concentrations measured at Station 1 was much lower than
the experimental variance obtained for the method in the laboratory (Table 1),
even though the variance for Station 1 was obtained for measurements on the
different samples obtained from different depths and includes the variation
in lead concentration with depth. This statistically significant difference
shows that the lead analyses carried out on HMAS KIMBLA were more precise than
those carried out, apparently under better conditions, in the laboratory. This
greater precision could reflect either the different physical state of the
electrode [47] or a lower level of airborne contamination on the ship [48].

Zirino [49] has suggested that the efficiency with which trace metals
are maintained at low levels in the mixed layer varies with the particular
trace metal. If oceanic circulation is rapid when compared to the net input
rate of material at the surface, mixing tends to homogenize the component and
leads to a distribution with little variation from surface to sediment. No
concentration profile would exist for very long in oceans with only surface
removal and no source of supply. Zirino suggested that Zn, Cu, Sb and Ni
would have lower than average concentrations in the upper 500 m compared to
deeper waters in the absence of aerosol input. Other elements such as lead
and possibly mercury had higher concentrations at shallow depths. The data
presented in this paper are insufficient in both quantity and precision to
support these suggestions. Also, Zirino and Yamamoto [50] have suggested
that the efficiency of removal of a material from the mixed layer is related
to the biological and thermodynamical stabilities of the chemical species of
that material in seawater, and to the flux of particulate matter sinking out
of the mixed layer.

The heavy metal levels reported in this paper fall within the range
found by recent workers, as is shown in Table 9, indicating that the heavy
metal concentrations found at these two ocean stations were as expected, and
that the sampling and analytical procedures were satisfactory. Published
data in this field have indicated that the currently used analytical pro-
cedures for heavy metals at the $\mu g.1^{-1}$ concentration level have a relative
standard deviation of the order of 50% for replicate analyses performed
within a laboratory [51].

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5.2 Other Parameters

As stated in the previous section, the only relationship found between heavy metal concentrations and the other parameters measured was a correlation between the Mg/Cl ratios and zinc concentrations at station 1, which is attributed, in the absence of any other evidence linking these two parameters, to chance. Hence the salinity, temperature, pH, dissolved oxygen, total alkalinity and magnesium measurements will be considered separately from the heavy metals measurements.

Examination of the variance ratios (Table 6) shows that the only significant difference in variability of these parameters with location or depth was in pH, which was significantly more variable in water type A at station 2 than in water type B. The variance ratio results also confirmed that the methods used to measure total alkalinity and Mg/Cl ratio were sufficiently sensitive to detect variations in these parameters at the two stations. The total alkalinity method [35,36] was designed principally for use in coastal waters and it was necessary to check that it was sufficiently sensitive for these measurements.

The variations in Mg/Cl ratio were of the same order of magnitude as those found elsewhere by atomic absorption spectroscopy [24], but not by titrimetric methods [25]. Continuing investigations [61] have established that variations observed off the East Australian coast are a function of the sample and are not due to random experimental error. It is suggested [61] that these variations could be due to differences in the forms in which magnesium is present in the samples. Differences in the form in which magnesium is present in seawater could also explain the variations in sound attentuation in seawater at frequencies below 100 kHz [19,20].

The statistical comparison of means (Table 5) shows the expected differences with depth of temperature, salinity, dissolved oxygen, percentage saturation of dissolved oxygen, pH and magnesium concentrations. The only statistically significant difference in means between the two stations was the higher mean pH in the surface waters at station A, which is discussed further below.

Examination of the correlation coefficients listed in Table 7 showed a number of correlations between different pairs of parameters, which are summarized in Figures 2, 3 and 4.

The absence of correlations in Figure 4 (despite their presence in Figures 2 and 3) between temperature and depth, pH and depth, pH and salinity and percentage dissolved oxygen saturation and salinity is explained by Table 8, which shows that the relationships between these parameters are different at the two stations. Thus, the correlations are destroyed when all of the data are combined.

In an attempt to explain the differences between the two stations, and to improve the degree of correlation between the various parameters, the degree of correlation was examined for different depth ranges and water types. The only positive conclusion drawn was that percentage dissolved oxygen saturation and pH were more closely correlated in the surface waters (type A) at both stations. Graphical plots showed no systematic variations from linearity in the relationships between any of the correlated parameters, indicating that

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the use of a non-linear expression would not improve the "closeness of fit" obtained with the linear regression equation. The quantitative relationships derived by linear regression analysis for correlated parameters are shown in Table 10. In addition, a number of 3-factor regression analyses were carried out for various combinations of correlated parameters, but in every case the degree of correlation was reduced.

The results show that all the parameters primarily affecting the degradation of materials in the marine environment are inter-related, except for total alkalinity and hence the carbon dioxide concentration. Thus these parameters can be regarded as having a composite effect on immersed materials which can be calculated from the relationships in Table 10 and knowledge of the chemical reactions involved. The task of predicting or explaining differences in the behaviour of submerged materials is thus greatly simplified because the ranges of values of the different parameters which must be considered, once a value has been assigned to one parameter, are restricted to the confidence limits listed in the table. The results show that it is inherently feasible to predict the rate of chemical degradation of a material and also the variation of this rate with changes in depth or other parameters. The significant differences in the relationships between some of these parameters between the two stations, which are little more than 100 nautical miles apart, demonstrate that hydrological features must be taken into account when making such predictions. Temperature structure off the East Australian coast is more closely linked with the circulation pattern than with season or geographical position [13]. Further studies are in progress to determine the extent to which the relationships between the parameters change in the presence or absence of the thermal eddies which are the main feature of the East Australian current. Considerable progress has been made [11,12,14] in understanding and modelling the circulation of the East Australian current, so it is hoped that the results of these dynamic studies can be combined with the chemical studies to predict chemical conditions in these waters.

It is interesting to note that the relationships between temperature and salinity are appreciably different at the two stations. Studies in the S.E. Indian Ocean have shown that salinity can be derived from temperature data [5]. In contrast to these studies, exclusion from the regression analysis of the data obtained for the surface mixed layer reported in this paper did not improve the degree of correlation, except for pH and per cent saturation of dissolved oxygen, where the relationship differed somewhat for surface and deeper waters. Dynamic height anomaly calculations off the East Australian coast [13] assume a constant T-S relationship. The success of assuming a constant T-S relationship in circulation studies is due largely to the fact that temperature is the main factor governing seawater density in low and middle latitudes [5] and the error involved in making this assumption is acceptable.

The rate of degradation of antifouling coatings has been estimated to increase by 4% for each $^{\circ}$C rise in temperature, 100% for each 0.1 unit decrease in pH, to be directly proportional to the dissolved oxygen (D.O.) concentration, and to increase proportionally with the square of the chloride concentration [3]. Applying these relationships to the range of measured values listed in Table 3, it can be seen that the rate of degradation would change 95% over the temperature range, 430% with the pH change, 41% with the change in D.O. concentrations and 7% with the change in salinity. Thus it

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can be seen that pH and temperature are the most important parameters affecting antifouling coatings in this area. Although total alkalinity only varies by 6%, it must be remembered that the carbon dioxide-carbonate-bicarbonate equilibrium in seawater depends on pH [35] - the concentration of free carbon dioxide varying by over 300% as a result.

Temperature and pH variations produce up to 50% variation in the concentration of the boron complex $(B(OH)_3)$ which is the prime cause of acoustic absorption in the 10 kHz frequency region [21,62,63,64]. Higher attenuation in the South Pacific Ocean, originally attributed to larger scattering loss, has been explained on the basis of such variations [63]. Normally, only temperature and salinity variations among the parameters described in this paper are taken into account when considering underwater acoustic propagation and it would be convenient if pH, temperature and salinity bore constant relationships to each other so that acoustic absorption could be considered as a temperature-salinity effect. Although Table 8 indicates that the pH-T relationship does not vary significantly at the two stations, the pH-depth and pH-S relationships are significantly different.

Variations in pH can be expected as a result of biological activity and the associated organic decomposition of organic matter to carbon dioxide and nitric acid [17,65]. The relationships between pH and percentage saturation of dissolved oxygen reflect the utilization of oxygen in this process. Differences in biological activity could account for the greater variability in pH in the surface (type A) waters at station 2 compared with the deeper (type B) waters and for the significantly higher pH in the surface waters at station 2 compared with the surface waters at station 1. A higher and/or more variably distributed biomass in the surface waters of station 2 would also account for the greater variability of lead and copper levels, and their correlation to each other.

The use of linear regression equations to describe the relationships between the different parameters measured implies a uniform rate of change of properties, whereas ocean waters in the western South Pacific consist of up to eight different water masses overlying each other [6]. To some extent assumption of a uniform rate of change is justified because mixing occurs between these strata, but departures from linearity must be expected. The correlations found between depth and temperature, salinity, dissolved oxygen, saturation and pH show that a reasonably uniform gradation occurs. A second reason why any equation is unlikely to describe exactly the relationships between these parameters is the possible presence and sampling of anomalous strata in the water column [8]. The errors listed in Table 10 reflect partly this situation and partly the small number of data sets in this study, but deviations from a linear relationship must always be expected. However, the purpose of the present approach is to define chemical conditions at any depth in the water column more closely than can be predicted from a knowledge of the water masses present. In terms of the water masses and nomenclature proposed by Wyrtki [6] for the Western South Pacific Ocean, water type A in this report is Subtropical Lower Water, while water type B is Antarctic Intermediate Water and water type C is a combination of Deep Oxygen Minimum Water and Deep Water. Thus, it is known from Wyrtki's classification what variations in salinity, temperature and dissolved oxygen concentration are to be expected within these water masses. The present approach enables values of these parameters to be defined for given depths,

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describes the relationships between them in quantitative terms, and enables pH to be predicted. Thus, it is complementary to studies on water mass distribution [6] which should, however, enable the results of chemical studies in one location to be used to predict conditions at other locations with some degree of confidence.

6. CONCLUSIONS

The concentrations of cadmium, copper, lead and zinc measured are typical of those found by other workers in other ocean areas.

The concentration of cadmium in all samples was less than 0.2 μgl^{-1}, the copper concentration varied between 0.4 and 4.8 μgl^{-1}, the lead concentration between 0.2 and 1.9 μgl^{-1} and the zinc concentration between 0.4 and 7.6 μgl^{-1}. The variations in concentration with depth and location found were within the experimental error of the anodic stripping voltammetry method used, except for variations in copper concentration in the surface waters of Station 2 which were significantly larger than at Station 1 or in deeper waters.

Comparison of variances showed that the sensitivity of the lead determinations at Station 2 was significantly greater than that measured ashore, even though variances calculated from the results obtained on board ship incorporate the variations to be expected from different samples obtained from different depths, compared with the replicate analyses on a single sample carried out ashore, and the results at sea were also obtained under apparently more unfavourable working conditions. The variations in lead concentration in the surface waters of Station 2 were correlated with the variations in copper concentration. Thus, anodic stripping voltammetry was sensitive enough to measure larger than normal variations in the levels of these metals in oceanic waters under favourable conditions. The correlated variations in copper and lead in the surface waters at Station 2 was associated with a greater variability in pH than occurred at Station 1 or in deeper waters. It is concluded that the most probable cause of these variations is the presence of a larger and/or more irregularly distributed biomass than that found in the surface waters at Station 1.

It was concluded from T-S and dissolved oxygen-S plots that three water masses or types were present at the two stations, and this conclusion was confirmed by the statistical comparison of means. Water type B (depth range 580-930 m) differed from type A (0-380 m) with respect to salinity, density and temperature, while water type B differed from type C (1880-3570 m) with respect to temperature and density only. In terms of Wyrtki's classification of water masses [6], water type A is subtropical Lower Water, water type B is Antarctic Intermediate Water and water type C is a combination of Deep Oxygen Minimum Water and Deep Water. Statistical comparison of means showed that the only difference between the two stations in the mean values of the parameters measured was a higher mean pH in the surface waters at Station 1.

It was concluded from analysis of variance that the observed variations in Mg/Cl ratio were larger than could be accounted for by the experimental error of ±0.0003. The ratios varied from 0.0643 to 0.0659, the variations

being of the same order of magnitude as those found by previous workers using atomic absorption spectroscopy.

At both stations magnesium-temperature, magnesium-percent saturation of dissolved oxygen, salinity-depth, temperature-salinity, pH-temperature, pH-percent saturation of dissolved oxygen, percent saturation of dissolved oxygen-depth, percent saturation of dissolved oxygen-temperature, salinity-magnesium, temperature-depth, pH-depth, pH-salinity and percent dissolved oxygen-salinity measurements were correlated to each other. These relationships were best expressed by simple linear regression equations. The use of multiple regression and power-series relationships do not improve the closeness of fit. The correlations of temperature and pH with depth, and of pH and percent saturation of dissolved oxygen with salinity, differed significantly between the two stations, probably because of differences in the organic material present. Further studies are needed to link these differences with hydrological features, such as thermal eddies, existing off the East Australian coast. It is concluded from the existence of these correlations that it should be feasible, on the basis of further studies and a knowledge of the hydrological structure of East Australian waters, to predict and explain the behaviour of submerged materials and variations in acoustic attenuation in the 10 kHz region more precisely than is presently possible.

7. ACKNOWLEDGEMENTS

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T A B L E   1

REPLICATE ANALYSES BY ASV IN A SHORE LABORATORY FOR HEAVY METALS IN SEAWATER

Metal	Concn $\mu g.\ l^{-1}$	No. of Determinations	Variance
Cu	1.25	14	0.23
Pb	1.27	14	0.49
Zn	5.29	7	3.20
Cd	0.28	14	0.01

T A B L E   2

Depth (m)	Dissolved Oxygen ($cm^3\ dm^{-3}$)	Relative Saturation of D.O. (%)	pH (corrected for temp. and depth)	Total Alkalinity meqv. l^{-1}	Temp. °C	Salinity o/oo	Chlorinity o/oo (44)	σ_t (45)
Station 1								
0	4.49	94.1	8.24	2.19	24.52	35.35	19.57	23.78
74	4.32	84.9	8.19	2.16	20.80	35.68	19.75	25.09
130	4.81	91.6	8.22	2.24	19.05	35.65	19.73	25.52
320	4.33	78.2	8.12	2.23	16.44	35.38	19.58	25.97
580	4.41	68.49	8.14	2.21	9.38	34.72	19.22	26.88
780	-	-	8.06	2.30	6.51	34.49	19.09	27.11
930	4.16	58.73	7.92	2.23	5.35	34.48	19.09	27.26
Station 2								
0	-	-	8.27	2.23	24.67	35.49	19.64	23.84
50	4.50	95.1	8.29	2.23	24.92	35.48	19.64	23.76
130	4.81	96.1	8.25	2.24	21.69	35.68	19.75	24.84
380	4.56	86.4	8.25	2.28	18.77	35.63	19.72	25.58
1880	3.42	45.1	7.93	2.28	2.60	34.65	19.18	27.67
2760	4.12	53.2	7.86	2.23	1.77	34.63	19.17	27.22
3570	4.32	55.3	7.95	2.23	1.30	34.80	19.26	27.90

T A B L E   3

MAGNESIUM, COPPER, LEAD, ZINC AND CADMIUM CONCENTRATIONS

Accepted Depth (m)	Magnesium concn (mg l^{-1})	Mg : Cl ratio (calcd)	Cu μg l^{-1}	Pb μg l^{-1}	Zn μg l^{-1}	Cd μg l^{-1}
Station 1						
0	1279	0.06536	0.9	0.9	7.6	< 0.2
74	1294	0.06552	0.5	0.5	5.5	< 0.2
130	1277	0.06472	1.5	0.8	4.0	< 0.2
320	1270	0.06485	-	-	-	-
580	1237	0.06437	< 0.5	0.6	0.4	< 0.2
780	1255	0.06574	-	-	-	-
930	1242	0.06507	0.5	0.5	5.1	< 0.2
Station 2						
0	1293	0.06582	4.8	1.9	5.5	< 0.2
50	1286	0.06548	0.5	0.7	9.1	< 0.2
130	1299	0.06577	-	-	-	-
380	1290	0.06541	0.9	0.7	2.6	< 0.2
1880	1234	0.06434	0.4	< 0.2	2.3	< 0.2
2760	1247	0.06506	2.3	0.6	3.3	< 0.2
3570	1269	0.06588	0.4	0.3	1.0	< 0.2

T A B L E 4

SUBDIVISION OF SEAWATER SAMPLES INTO TYPES ON BASIS OF SALINITY,
TEMPERATURE, DISSOLVED OXYGEN AND DEPTH DATA

Water Type	Max./Min.	Depth Range (m)	σ_t	Temp. ($^\circ$C)	Salinity ($^\circ$/oo)	Dissolved Oxygen ($cm^3 dm^{-3}$)
A	min.	0	23.76	18.77	35.35	4.33
	max.	380	25.97	24.92	35.68	4.81
B	min.	580	26.88	5.35	34.48	4.28
	max.	925	27.26	9.38	34.72	4.41
C	min.	1880	27.67	1.30	34.63	3.42
	max.	3570	27.90	2.60	34.80	4.32

T A B L E 5

COMPARISON OF MEANS USING 't' OR 'd' TEST

Data Sources (1)	(2)	Calcd. t or d	Degrees of Freedom	% Probability of Difference	Mean Value (1)	Mean Value (2)
Temperature (^{o}C)						
1A	2A	1.036	6	< 70	20.20	22.51
A	B	7.123	9	> 99.9	21.36	7.08
B	C	4.130	4	> 98	7.08	1.89
Salinity (^{o}/oo)						
1A	2A	0.566	6	< 50	35.51	35.57
A	B	10.785	9	> 99.9	35.54	34.46
B	C	1.355	4	< 80	34.56	34.69
σ_t						
1A	2A	0.912	6	< 70	25.09	24.51
A	B	4.243	9	> 99	24.80	27.08
B	C	5.202	4	> 99	27.08	27.76
Dissolved Oxygen (cm^3 dm^{-3})						
1A	2A	0.865	5	< 60	4.49	4.62
A	B	1.640	7	< 90	4.55	4.29
B	C	0.910	3	< 60	4.29	3.95
A	C	2.925	8	> 98	4.55	3.95
Relative Saturation of Dissolved Oxygen (%)						
1A	2A	1.077	5	< 70	87.2	92.5
A	B	4.875	7	> 99	89.5	63.6
B	C	2.295	3	< 90	63.6	51.2
A	C	8.820	8	> 99.9	89.5	51.2

COMPARISON OF MEANS USING 't' OR 'd' TEST

Data Sources (1) (2)		Calcd. t or d	Degrees of Freedom	% Probability of Difference	Mean Value (1)	Mean Value (2)
pH						
1A	2A	2.478	6	> 95	8.19	8.26
1A	B	2.443	5	< 95	8.19	8.04
2A	B	1.957	4.3	< 95	8.26	8.04
1A	C	7.254	5	> 99	8.19	7.91
2A	C	13.686	5	> 99.9	8.26	7.91
Total Alkalinity (milliequivalents per litre)						
1A	2A	1.750	6	< 90	2.21	2.24
A	B	0.853	9	< 60	2.23	2.25
A	C	0.935	9	< 70	2.23	2.25
1	2	1.182	12	< 80	2.22	2.25
Magnesium (mg l^{-1})						
1A	2A	2.089	6	< 95	1280	1292
A	B	6.258	9	> 99.9	1286	1245
A	C	4.408	9	> 99	1286	1250
Mg:Cl Ratio						
1A	2A	2.315	6	< 95	0.06511	0.06562
A	B	0.952	9	< 70	0.06537	0.06506
A	C	0.801	9	< 60	0.06537	0.06509
1	2	1.105	12	< 80	0.06509	0.06539

COMPARISON OF MEANS USING 't' OR 'd' TEST

Data (1)	Sources (2)	Calcd. t or d	Degrees of Freedom	% Probability of Difference	Mean Value (1)	Mean Value (1)
Copper ($\mu g l^{-1}$)						
1A	2A	0.785	4	< 60	1.0	2.1
1A	B	1.53	3	< 80	1.0	0.4
2A	C	0.684	4	< 50	2.1	1.0
1	2	0.45	4,5	< 95	0.7	1.6
Lead ($\mu g l^{-1}$)						
1A	2A	0.878	4	< 60	0.7	1.1
1A	B	1.149	3	< 70	0.7	0.6
2A	C	1.801	4	< 90	1.1	0.3
1	2	0.087	4,5	< 95	0.7	0.7
Zinc ($\mu g l^{-1}$)						
1A	2A	0.0155	4	< 10	5.7	5.7
1A	B	1.355	3	< 80	5.7	2.8
2A	C	1.772	4	< 90	5.7	2.2
1	2	0.326	9	< 30	4.5	4.0

T A B L E   6

'F' RATIOS

Data Source Numerator	Denominator	Degrees of Freedom Numerator	Denominator	F Ratio	% Probability Of Difference
Temperature					
1A	2A	3	3	1.37	< 50
A	B	7	2	2.33	< 50
B	C	2	2	9.94	< 90
Salinity					
1A	2A	3	3	2.98	< 80
B	A	2	7	1.02	< 50
B	C	2	2	2.01	< 50
σ_t					
1A	2A	3	3	1.18	< 50
A	B	7	2	21.9	92
B	C	2	2	2.5	< 50
Dissolved Oxygen					
1A	2A	3	2	1.39	< 50
A	B	6	1	1.29	< 50
C	B	2	1	7.15	< 50
C	A	2	6	5.52	91
Relative Saturation of Dissolved Oxygen					
1A	2A	3	2	1.79	< 50
B	A	1	6	1.11	< 50
B	C	1	2	1.66	< 50
A	C	6	2	1.50	< 50

T A B L E   6

(Continued)

'F' RATIOS

Data Source Numerator	Denominator	Degrees of Freedom Numerator	Denominator	F Ratio	% Probability Of Difference
pH					
1A	2A	3	3	6.84	< 90
B	1A	2	3	4.50	< 80
B	2A	2	3	31.0	> <u>98</u>
1A	C	3	2	1.28	< 50
C	2A	2	3	5.36	< 80
Total Alkalinity					
1A	2A	3	3	2.67	< 80
B	A	2	8	1.59	< 50
A	C	7	3	1.35	< 50
1	2	6	6	3.21	< 90
1	L	6	3	74.0	> <u>98</u>
2	L	6	3	23.0	> <u>95</u>
Magnesium					
1A	2A	3	3	3.4	< 80
A	B	7	2	1.13	< 50
C	A	2	7	3.20	< 80
Mg:Cl Ratio					
1A	2A	3	3	3.57	< 80
B	A	2	7	3.01	< 80
C	A	2	8	3.81	< 90
2	1	6	6	1.25	< 50
1	L	6	9	19.7	> <u>99.8</u>
2	L	6	9	25.3	> <u>99.8</u>

T A B L E   6

(Continued)

'F' RATIOS

| Data Source | | Degrees of Freedom | | F | % Probability |
Numerator	Denominator	Numerator	Denominator	Ratio	Of Difference
Copper					
2A	1A	2	2	53.9	<u>95</u>
1A	1B	2	1	3.35	< 50
2A	2C	2	2	4.69	< 80
2	1	5	4	12.8	<u>97</u>
1	L	4	13	1.04	< 50
2	L	5	13	13.3	> <u>99.8</u>
Lead					
2A	1A	2	2	11.1	< 90
1A	1B	2	1	8.58	< 80
2A	2C	2	2	7.58	< 80
2	1	5	4	11.9	<u>96</u>
L	1	13	4	14.8	> <u>98</u>
L	2	13	5	1.24	< 50
Zinc					
2A	1A	2	2	3.24	< 80
1B	1A	1	2	3.38	< 50
2A	2C	2	2	7.97	< 80
2	1	5	4	1.22	< 50
1&2	L	9	6	2.45	< 80

T A B L E 7

CORRELATION COEFFICIENTS FOR PAIRED PARAMETERS

Note: Upper-right triangle = STATION 2; lower-left triangle = STATION 1. Each cell gives the correlation coefficient with the number of pairs in parentheses.

	Depth	Temp.	Sal.	D.O.	D.O. Saturation	pH	Total Alk.	Mg	Mg:Cl	Cu	Pb	Zn
Depth		0.9492 (7)	0.8858 (7)	0.4961 (6)	0.8712 (6)	0.9244 (7)	0.1180 (7)	0.3057 (7)	0.2298 (7)	0.3576 (6)	0.6228 (6)	0.7120 (6)
Temp.	0.9860 (7)		0.9408 (7)	0.7141 (6)	0.9774 (6)	0.9816 (7)	0.1506 (7)	0.8641 (7)	0.5001 (7)	0.3790 (6)	0.7137 (6)	0.7681 (6)
Sal.	0.9374 (7)	0.9104 (7)		0.8113 (6)	0.9698 (6)	0.9715 (7)	0.0309 (7)	0.4093 (7)	0.5837 (7)	0.2501 (6)	0.6149 (6)	0.5554 (6)
D.O.	0.5924 (6)	0.5139 (6)	0.5707 (6)		0.8448 (6)	0.7244 (7)	0.4292 (6)	0.9459 (6)	0.8859 (6)	0.0658 (5)	0.8307 (5)	0.3481 (5)
D.O. Saturation	0.9724 (6)	0.9664 (6)	0.8859 (6)	0.7158 (6)		0.9659 (6)	0.1184 (6)	0.9308 (6)	0.5807 (6)	0.1914 (5)	0.8064 (5)	0.7075 (5)
pH	0.9203 (7)	0.8637 (7)	0.7930 (7)	0.7195 (6)	0.9134 (6)		0.0699 (7)	0.2737 (7)	0.5357 (7)	0.2597 (6)	0.6319 (6)	0.6676 (6)
Total Alk.	0.6207 (7)	0.6337 (7)	0.5820 (7)	0.2376 (6)	0.3115 (6)	0.4510 (7)		0.3069 (7)	0.6793 (7)	0.4246 (6)	0.4403 (6)	0.3705 (6)
Mg	0.8661 (7)	0.8723 (7)	0.8946 (7)	0.3475 (6)	0.8373 (6)	0.6933 (7)	0.4922 (7)		0.8255 (7)	0.3274 (6)	0.6744 (6)	0.4702 (6)
Mg:Cl	0.0211 (7)	0.0894 (7)	0.0415 (7)	0.2873 (6)	0.3541 (6)	0.0686 (7)	0.0919 (7)	0.4093 (7)		0.3383 (6)	0.5530 (6)	0.1936 (6)
Cu	0.5252 (5)	0.5251 (5)	0.6120 (5)	0.8461 (5)	0.6863 (5)	0.4642 (5)	0.4175 (5)	0.4848 (5)	0.0134 (5)		0.9067 (6)	0.2080 (6)
Pb	0.6117 (5)	0.6470 (5)	0.4173 (5)	0.7389 (5)	0.7462 (5)	0.6594 (5)	0.1954 (5)	0.3177 (5)	0.0276 (5)	0.7058 (5)		0.4471 (6)
Zn	0.4397 (5)	0.5888 (5)	0.3915 (5)	0.0762 (5)	0.4752 (5)	0.1363 (5)	0.3130 (5)	0.6333 (5)	0.8861 (5)	0.3362 (5)	0.3452 (5)	

T A B L E 8

INTER-STATION COMPARISON OF REGRESSION COEFFICIENTS

y	x	t	Total degrees of freedom	% Probability of difference
Mg	Temp	0.614	12	< 50
Mg	% DO	0.709	10	~ 50
Sal	Depth	1.4	12	< 90
Temp	Sal	0.0998	12	< 10
pH	Temp	1.13	12	< 90
pH	% DO	0.127	10	< 10
% DO	Depth	2.12	10	< 95
% DO	Temp	0.591	10	< 50
Sal	Mg	1.18	12	< 90
Temp	Depth	4.12	12	> 99
pH	Depth	2.20	12	> 95
pH	Sal	3.05	12	~ 99
% DO	Sal	2.36	10	> 95

TABLE 9

COMPARISON OF TRACE ELEMENT CONCENTRATION FOUND IN
RECENT INVESTIGATIONS

Reference		Metal Concentration ($\mu g. \ l^{-1}$)			
		Cd	Cu	Pb	Zn
Station 1	range	<0.2	3.5-<0.5	0.5-0.9	0.4-7.6
	mean	<0.2	0.7	0.7	4.5
Station 2	range	<0.2	4.8-0.4	0.2-1.9	1.0-9.1
	mean	<0.2	1.6	0.7	4.0
Kremling and Petersen (52)		0.12	1.4	-	5.6
Eaton (53)		0.06	-	-	-
Bruland, Knauer and Martin (54)		0.004-0.06	-	-	-
Schaule and Patterson (55)		-	-	0.014	-
Nurnberg et al. (56) (Bay of La Spezia)		0.02-0.08	-	0.07-1.1	-
Florence and Batley (31)		-	-	0.3-1.0	-
Florence (30)		0.19-1.06	0.93-9.8	0.33-1.91	2.82-6.5
Chester and Stoner (57) (Indian Ocean)		0.05-0.07	0.6	-	1.4
Knauer and Martin (58)		N.D.-0.06	0.4-1.2	N.D.-0.7	0.8-2.5
Preston et al. (59) (Irish Sea)		0.03-1.43	0.9-2.7	0.9-2.9	4.9-11.1
Boyle and Edmond (60) (N.Z. Coastal Waters)		-	0.98-3.3	-	-

T A B L E   10

RESULTS OF LINEAR REGRESSION ANALYSES FOR CORRELATED PAIRED
PARAMETERS AT THE TWO STATIONS (y = ax + b)

x	y	a	b	St. dev. (σ)	±error in y (calcd from σt) (pr = .05)
Station 1					
D	T	−0.02024	22.71	1.370	3.52
D	S	−0.001357	35.65	0.2021	0.519
D	%DO	−0.03762	92.06	3.583	9.96
D	pH	−0.0002808	8.239	0.04786	0.123
D	Mg	−0.04945	1284.7	11.44	29.4
T	S	0.06422	34.169	0.2400	0.617
T	%DO	1.833	50.14	3.947	10.97
T	pH	0.01284	7.938	0.06164	0.158
T	Mg	2.427	1229.5	11.19	28.8
S	%DO	24.48	−782.6	7.126	19.8
S	pH	0.1671	2.258	0.07451	0.192
S	Mg	35.28	26.14	10.23	26.3
%DO[a]	pH[a]	0.007295	7.556	0.01257	0.0540
%DO[b]	pH[b]	0.007851	7.514	0.05376	0.154
%DO	Mg	1.364	1158.3	13.68	38.0
Station 2					
D	T	−0.007214	22.71	3.865	9.93
D	S	−0.002873	35.55	0.2434	0.625
D	%DO	−0.01345	91.52	12.71	35.3
D	pH	−0.0001194	8.261	0.07965	0.205
T	S	0.04015	34.64	0.1779	0.457
T	%DO	2.041	47.40	5.471	15.7
T	pH	0.01668	7.883	0.03988	0.103
T	Mg	2.374	1245.9	15.70	49.9

T A B L E 10

(Continued)

x	y	a	b	St. dev. (σ)	±error in y (calcd from σt) (pr = .05)
S	DO	0.7789	−23.08	0.3167	0.880
S	%DO	44.46	−1490.7	6.306	17.5
S	pH	0.3867	−5.499	0.04950	0.127
*S	Mg	48.17	−421.9	11.64	37.0
%DO	DO	0.01769	3.017	0.2899	0.806
DO	Mg	49.27	1058.6	10.38	33.02
%DO[a]	pH[a]	0.002064	8.069	0.003058	0.389
%DO[b]	pH[b]	0.008115	7.502	0.05630	0.157
%DO	Mg	1.036	1196.4	10.53	29.3
Mg/Cl	Mg	0.00001806	0.04239	0.0003377	0.00868

* 130–3570 m depth range

[a]Stn 1; 0–320 m   .Stn 2; 50–380 m depth range
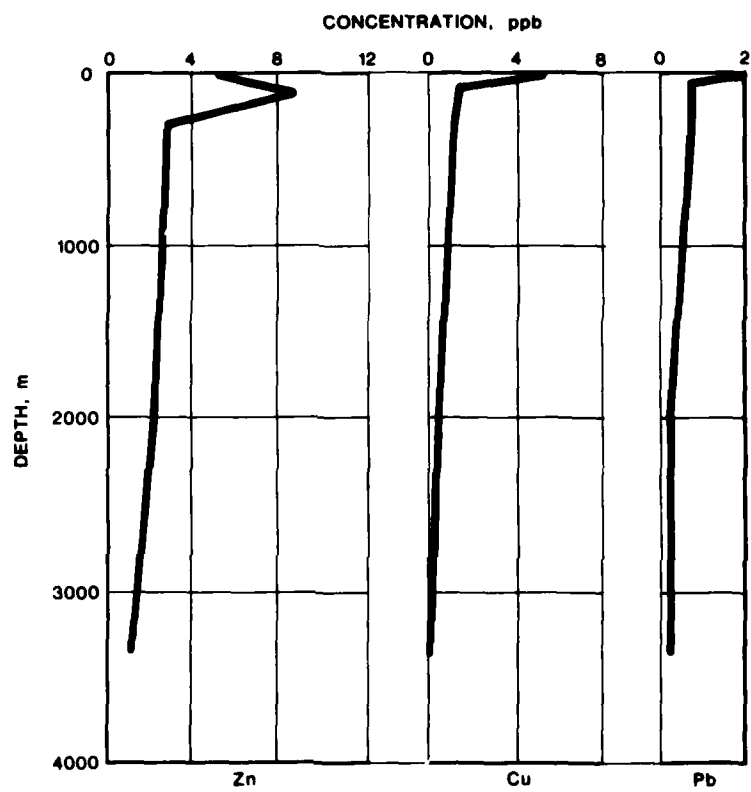
[b]Stn 1; 0–930 m   .Stn 2; 50–3570 m depth range.
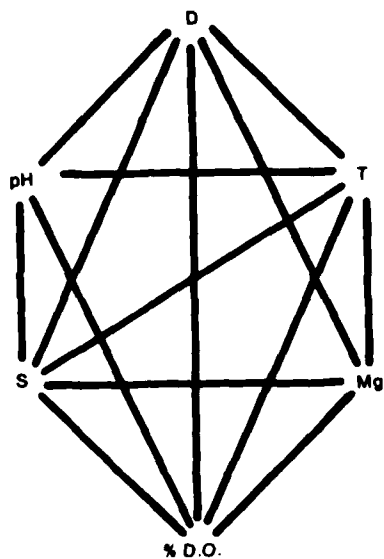
FIG. 1 - Heavy metal concentrations at Station 2.

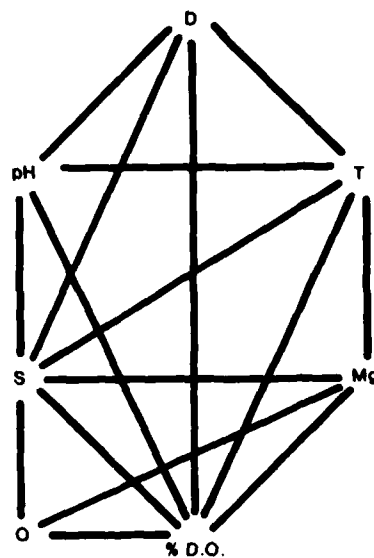FIG. 2 - Correlation diagram for
parameters measured at Station 1
(pr ≤ 0.05)

FIG. 3 - Correlation diagram for
parameters measured at Station 2
(pr ≤ 0.05)
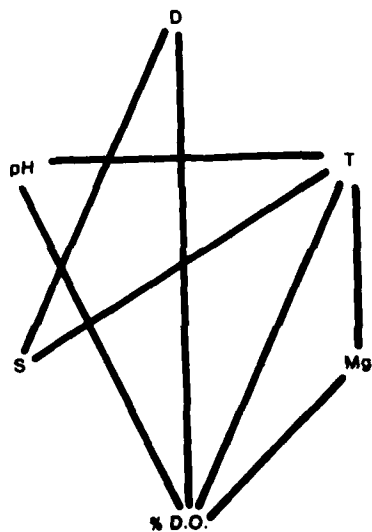
FIG. 4 - Correlation diagram for parameters
measured at Stations 1 and 2, combined
(pr < 0.05). (Correlation coefficients not
included in the paper).

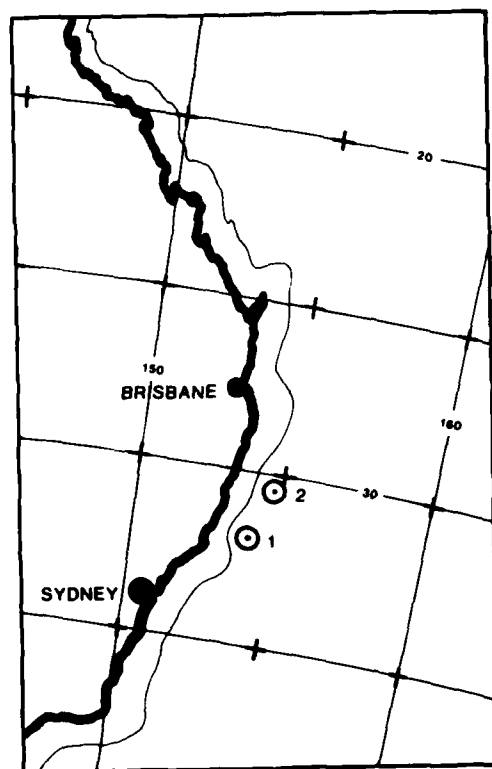FIG. 5 - Location of sampling stations.

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